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LONG-TERM CYCLING OF THE MAGNESIUM HYDROGEN SYSTEM

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Abstract—Magnesium powder with a grain size of approximately $50\text{ }\mu\text{m}$ was hydrogenated for 30 min and dehydrogenated the same time at 390°C , 515 times. A moderate loss in hydrogen storage capacity was observed and was ascribed to a measured decrease in reaction kinetics as the cycle number increased. The time for maximum hydrogen absorption was found to depend significantly on cycle number while the time for maximum desorption was found to be virtually independent of cycle number.

INTRODUCTION

The technological and scientific interest in metals as hydrogen storage systems has increased during the last decennium. However, many of those systems which are generally considered most promising suffer from materials shortages or high prices (e.g. LaNi_5 , Mg_2Ni , FeTi). On this ground it is natural that especially the cheap and abundant magnesium has attracted still more attention, in spite of some early, quite negative results on the hydrogenation/dehydrogenation of this metal [1]. It has been demonstrated [2] that finely comminuted magnesium metal (in powder form with a grain size of approximately $50\text{ }\mu\text{m}$ or less) readily absorbs hydrogen without any noticeable activation process. Likewise it has been demonstrated [3-4] that magnesium hydride just as readily dissociates to reform the starting materials: magnesium and hydrogen.

If the magnesium-hydrogen system is to be of any practical importance it is essential that the system can undergo the cyclic metamorphosis of the hydrogenation and dehydrogenation sufficiently many times to economically justify the utilization. Exactly how many times this means cannot be said unconditionally. The number will depend on many factors like materials prices, storage times, the application in question, etc. It is the aim of the present paper to report our findings on cycling of the magnesium hydrogen system 500 times.

AUTOMATIC CYCLING APPARATUS

In order to complete a great number of hydrogenation cycles within a short time we built an automatic cycling equipment controlled by a microcomputer. The equipment is described in detail elsewhere [5]. Here we shall just give an outline of the principles. Figure 1 shows a diagram of the equipment. The measuring technique is based on the measurement of pressure and temperature in known volumes. Before the start of a cycle, volume B was filled with hydrogen. Then the preheated oven was lowered to heat the sample to approx. 390°C . When the reaction temperature was reached, the three-way valve V2 was turned to allow the gas into the reaction chamber A. The pressure in A was kept con-

stant by the reduction valve RV throughout the reaction even though the pressure in B decreased. The pressure drop in B was used to calculate the amount of hydrogen taken up by the sample. After 30 min, V2 was closed and the oven elevated. When the sample had cooled down to 80°C the volumes A and D were evacuated to 10^{-2} bar, and then the oven was lowered to heat the sample to ca 390°C . At this temperature valve V2 was opened towards D and the increase in pressure during 30 min was measured to calculate the amount of hydrogen released. Finally the oven was elevated to complete the cycle. Figure 2 shows the correlated values of the temperature and three pressures PA, PB and PD during one full cycle.

Since the sample consisted of fine powder, it was necessary to construct a container which would prevent powder particles from spreading to the entire system with the expanding gas. The sample container was made of stainless steel and closed by a porous disc.

The pressures were measured by means of piezo-resistive transducers (Kistler) with an overall precision better than 1% (0-50 bar). The temperature was measured with a thermocouple (NiCr-Ni). Two points should be stressed in connection with the temperature measurement. First, we had an unfavorable temperature profile over the sample container in consequence of an inappropriate oven design. Since the powder tended to spread to all available volume, this means that the measured temperature was not accurately representative for the whole sample. As a consequence of this fact, we obtained misleading results in some cases

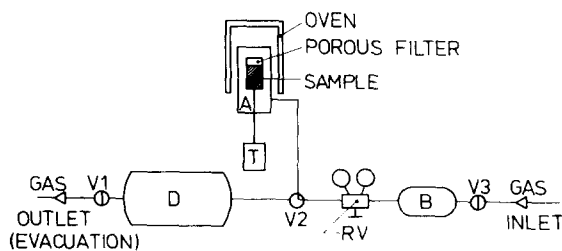


Fig. 1. Schematic diagram of the equipment.

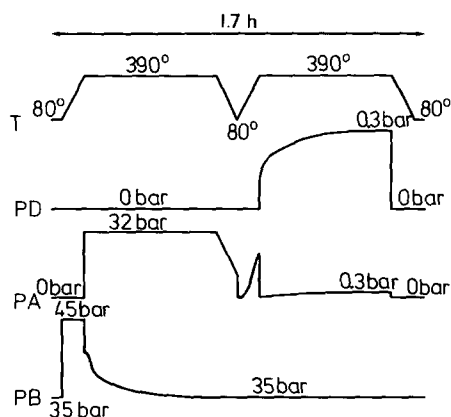


Fig. 2. Correlated values of the temperature and the pressures during one cycle.

(cf. the Results section). Secondly, the absorptions were all carried out at a formally constant temperature. It is well known that the heat of reaction causes the temperature within the individual grains to rise considerably during absorption and fall during desorption. For these reasons the significance of the measured temperature should not be overrated. We consider it merely one of those initial conditions determining the development of the reaction.

MATERIALS

For the cycling experiment we used hydrogen of 99.9997% purity, the main impurities being H_2O (2 ppm), N_2 (0.5 ppm) and O_2 (0.5 ppm). The gas was delivered by L'Air Liquide. The magnesium material used was a commercially available powder quality, supplied by Baudier, France. The powder was specified as 33–75 μm containing Si and Mn as the main metallic impurities, 1000 ppm each. The oxide content of the magnesium powder was determined by dissolving the MgO in 1N acetic acid and determination of dissolved magnesium by flame atomic absorption. Four independent analyses were made and showed 1.8, 2.4, 2.1 and

2.2% MgO. The analyses were carried out by Norsk Hydro Research Centre, Analysis Department.

RESULTS

A. Capacity

Figure 3 shows the amount of hydrogen stored within 30 min, as measured by the desorptions versus cycle number. The hydrogen was stored at 32 bar and approximately 390°C. It was released under vacuum (0–0.3 bar) at the same temperature. It should be noted that the anomalous behaviour seen in the ranges of cycle numbers 5, 60–75, 125–135 and 215–220 is caused by an inadvertent movement of the powder (within the sample holder) out of the zone of appropriate reaction temperature. If these specific results are disregarded, a steady decrease in the amount of stored hydrogen is observed as the cycle number increases. The decrease seems to become smaller with increasing cycle number, i.e. the second order derivative is positive. The amounts of stored hydrogen in the cycle number range 500–515 are large because of a prolonged reaction period. In these cycles the powder was allowed to react for 8 h, resulting in a considerably higher absorption capacity.

B. Kinetics

The amount of reacted hydrogen versus time is shown in Fig. 4 for the absorption and in Fig. 5 for the desorp-

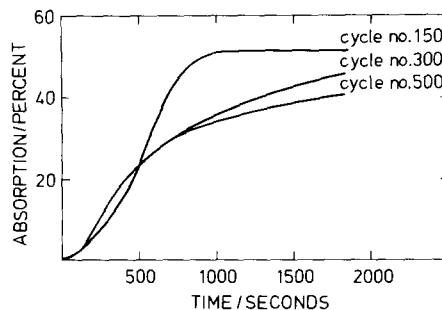


Fig. 4. Time-dependence of the hydrogen absorption (%).

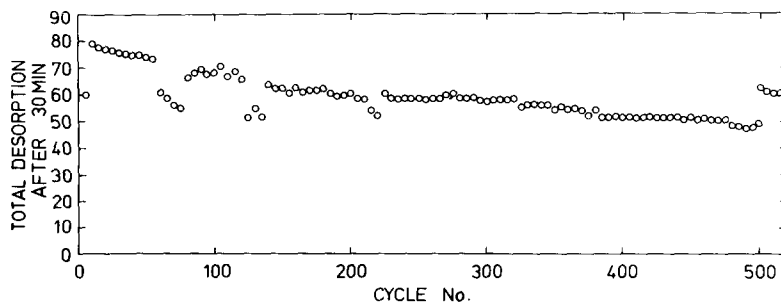


Fig. 3. Storage capacity (% of theoretically obtainable stoichiometry) versus cycle number.

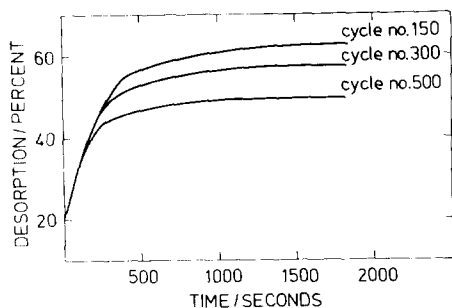


Fig. 5. Time-dependence of the hydrogen desorption (%).

tion. The figures illustrate the characteristic times for the reactions. The rate of reaction did not vary noticeably as a function of cycle number in the case of the desorption as indicated by Fig. 5. In contrast to this Fig. 4 shows for the absorption that 30 min was increasingly an insufficient time for the reaction to be completed as the cycle number increased.

C. Scanning Electron Microscopy

SEM micrographs of the powder taken at $300\times$ magnification are shown in Figs 6 and 7. As has been observed many times before, the morphology of the

sample has changed drastically as a result of the hydrogen treatment.

DISCUSSION

The fall in storage capacity shown in Fig. 3 can be partly explained by a continuous reaction between the magnesium powder and impurities in the hydrogen gas used for the experiment. Such a reaction will transform hydrogen-active magnesium metal into passive magnesium oxide (presumably magnesium nitride is not formed even though nitrogen is present in the hydrogen gas). Under the assumption that all available impurity gas in our experiment actually reacted with the magnesium powder, we calculated the impurity reaction to imply a maximum passivation of about 0.002% of the magnesium per cycle. Even if the calculation is in error by a factor of 10, it is obvious that the observed fall in storage capacity mainly occurs for other reasons. These reasons must be intimately connected with the materials' characteristic parameters or rather the change of them. Probably the most important reason for the observed fall in storage capacity is the slower kinetics with increasing cycle number. In the experiment the absorption was performed for 30 min and then stopped. As the rate of absorption decreases, this means that the total amount of hydrogen absorbed also decreases. The effect is simply a matter of non-equilibrated systems, as also indicated by the positive time-derivative at $t = 1800$ s

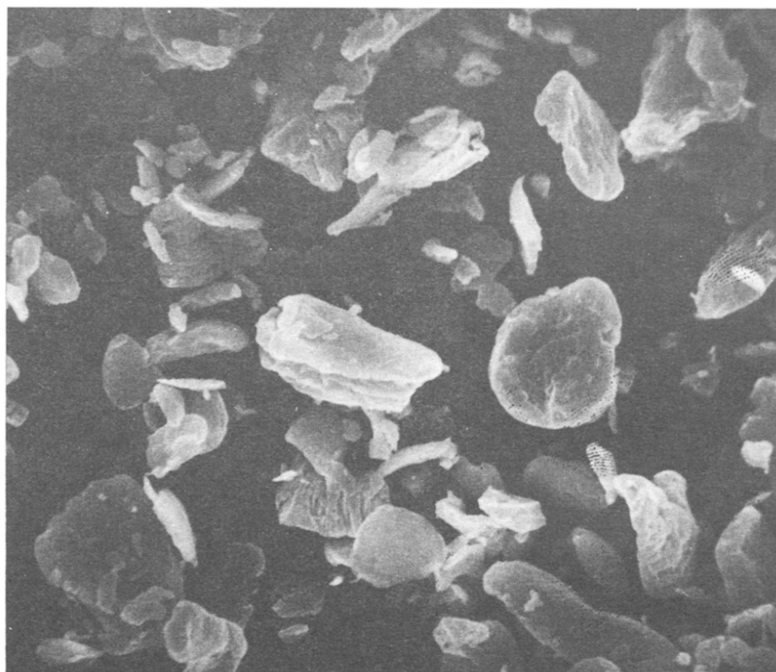


Fig. 6. Magnesium powder prior to hydrogen exposure, $300\times$.

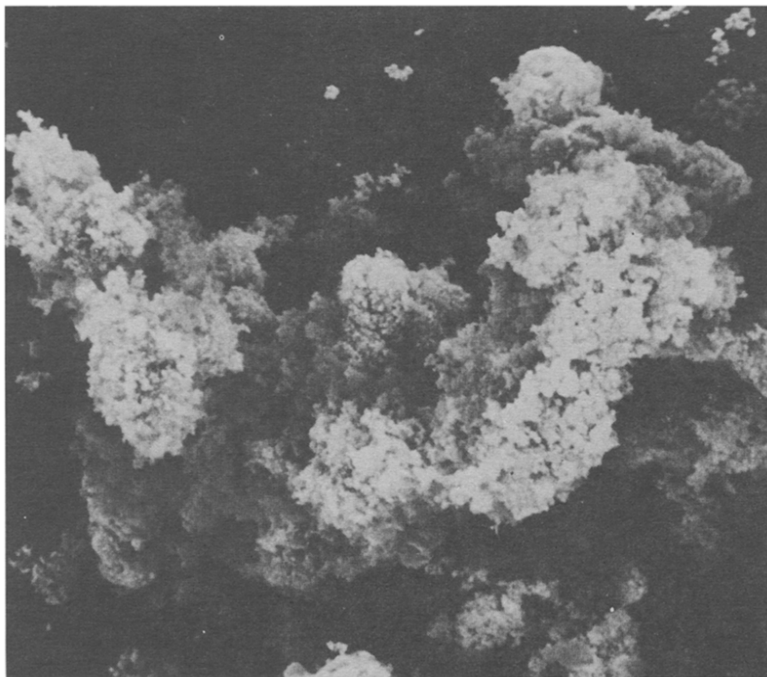


Fig. 7. Magnesium hydride after 515 cycles, 300 \times .

in Fig. 4. If the 30 min absorption is surpassed, as in cycles 500–515, a rather large increase in storage capacity is observed, making the capacity comparable with that at low cycle numbers.

At the present stage, the reason for the observed reaction rates is speculative. We tentatively suggest that grain growth takes place as a result of the high reaction temperatures (during absorptions above 400°C within individual particles). Since the hydrogen diffusion preferentially occurs in the grain boundaries, the recrystallization process disfavors the diffusion into the interior of the particles, thereby causing the observed effect on the absorption kinetics.

CONCLUSIONS

Magnesium powder with a grain size of approximately

40 μm or less is a suitable material for repeated storing of hydrogen. The loss in storage capacity during 500 cycles is small and is not a hindrance for the utilization of this material for energy storage purposes.

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